
MODERN
SUPERABSORBENT
POLYMER TECHNOLOGY

Edited by
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Preface

Acknowledgments

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Table 2.4. Comparison of polymerization rate measurements

Reference	T(°C)	pH	[M] ₀	Initiator type ^a	[I] ₀	$R_p/[M]^{3/2}[I]^{1/2}$
Manickam et al. ³⁸	50	1	0.138	KPS	0.01	0.491–0.586
	50	4.2	0.172		0.01	0.236
	50	11	0.258		0.01	0.091–0.444
Kabanov et al. ³²	60	1	1.2	AIBN	0.005	0.14
	60	10	1.2		0.005	0.19
	60	~7	1.2		0.005	0.00278
Ito et al. ³¹	50	2.4	0.5	APS	0.00285	0.90
	50	4.7	0.5		0.00285	0.14
	50	7.2	0.5		0.00285	0.045
Cutié et al. ²⁴	55	4.5	1.14–4.56	NPS	0.0023	0.126–0.239

^aKPS, potassium persulfate; AIBN, 2,2'-azobis(isobutyronitrile); APS, ammonium persulfate; NPS, sodium persulfate.

cation for a batch polymerization is that the molecular weight will likely decrease as the polymerization proceeds, because the rate of propagation decreases while termination and initiation remain relatively constant. In Figure 2.9 the cumulative molecular weight data from identical isothermal polymerizations at 55°C are plotted versus the extent of conversion, illustrating this point.³⁶ Two notes should be made of these data: (1) The molecular weight decreases significantly with conversion, which, while anticipated, confirms the likelihood of forming a low-molecular-weight fraction late in the polymerization; and (2) the molecular weight values are large compared with those for many other polymers. The unusually large molecular weight of many commercial acrylic acid (and acrylamide) polymers is utilized in the application of the soluble (uncrosslinked) polymers as viscosifiers and flocculants.⁴⁰ This is probably a reflection of their high propagation rates, compared with those for other monomers, rather than low termination or initiation rates. For example, from a comparison of chemical structures one might expect the polymerization of acrylic acid to proceed at a rate similar to that for methylacrylate. In fact, at 60°C the propagation of aqueous acrylic acid, as determined from rotating sector experiments,⁴¹ is faster than that of methylacrylate.²⁶ Results of Laborie⁴² and of Chapiro and Dulieu⁴³ suggest that the high value for the propagation rate results from an interesting templating effect at high concentrations due to hydrogen bonding with water. In aprotic solvents, without such hydrogen bonding, the rates are much lower.

2.5.3. Inhibition

As noted in section 2.2.2.1, commercial monomer grade acrylic acid typically contains 200 ppm MEHQ, and it is recommended that it be stored under an air atmosphere. This is a high level of inhibitor when compared with that used in other vinyl

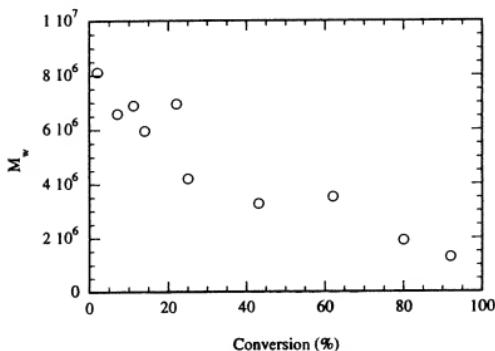


Figure 2.9. Effect of conversion on cumulative molecular weight (M^*). Polymerization was at 65% neutralization and 55°C.

monomers. Styrene, for example, is inhibited with 3–10 ppm of *tert*-butylcatechol. Reproducible polymerizations of acrylic acid generally begin with the deoxygenation of the system, and induction times vary roughly inversely with oxygen concentration.

The role of oxygen in the stability of vinyl monomers is complicated. For example, most purified vinyl monomers will not polymerize upon heating in the absence of oxygen (styrene being an exception), but virtually all vinyl monomers will readily form peroxides upon exposure to air. These peroxides have been found to break down and initiate polymerization at elevated temperatures.⁴⁴ At lower temperatures, where the peroxides are relatively stable, oxygen often reacts with other free radicals in the system, thereby functioning as an inhibitor. This delicate balance between inhibition and reinitiation is influenced by temperature, the oxygen content of the system, and the thermal stability of the peroxide formed from the particular monomer. In a closed system, oxygen is eventually depleted and polymerization proceeds. In contrast, when there is an unlimited supply of oxygen, such as in an open vessel, vinyl monomers will absorb a large quantity of oxygen, forming polyperoxides but not polymerizing.⁴⁵

Even trace amounts of oxygen in otherwise very pure systems can suppress the polymerization of acrylic or methacrylic acids. Blauer⁴⁶ reported that even the small amounts of oxygen remaining in *purified* nitrogen would retard the polymerization of methacrylic acid if continuously bubbled through the solution during the reaction. Levy⁴⁷ has shown that, in the absence of oxygen, there is no induction time at 100°C for MEHQ-inhibited acrylic acid, and no detectable amount of MEHQ is consumed or reacts with the polymer radicals. By continuously monitoring the oxy-

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gen level in the reaction vessel, Kurland⁴⁸ determined the oxygen consumption during polymerization of neat acrylic acid at 50°C containing relatively high (106 ppm) and low (1.7 ppm) levels of MEHQ. At the lower level, a rapid increase in the rate of oxygen consumption was observed once the MEHQ was depleted. Initially about six molecules of oxygen were consumed per initiator radical generated, but, when the MEHQ was depleted, about 32 molecules per radical were consumed. Regardless of the MEHQ content, polymerization occurred when the oxygen content was reduced to about 0.5 ppm, clearly showing that the polymerization is inhibited by oxygen, not MEHQ. The rate of oxygen consumption, however, is much slower in the presence of higher levels of MEHQ.

Levels of MEHQ ranging from 16 to 151 ppm have been found in commercial superabsorbent polymers, as indicated in Table 2.5. The amount of MEHQ that survives the polymerization process may be the result of the efficiency of deoxygenation, the reaction temperature, and, most important, the nature of the polymerization catalyst. Persulfates are more powerful oxidants than azo compounds and more efficient at hydrogen abstraction; they may therefore convert more of the MEHQ to quinone.^{24,49} The latter has been detected as a byproduct of the MEHQ-inhibited acrylic acid polymerization initiated with sodium persulfate.

The mechanism for inhibition/retardation presented in section 2.4.3 implies that, if the inhibition constant $z = k_i/k_p$ is large, significant polymerization will not occur until the species Z is completely consumed (induction period), after which time the rate is normal (inhibition). If the effect is milder (z is smaller), polymerization occurs from the outset but at a reduced rate (retardation).²⁶ MEHQ in acrylic acid may not fit cleanly into either category. In a study of the isothermal persulfate-initiated polymerization of acrylic acid at various MEHQ levels,²⁴ the initial observations were the following:

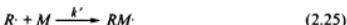
1. In deoxygenated runs, polymerization began almost immediately.
2. The rate was lowered by the addition of MEHQ.
3. MEHQ was found in the polymer after essentially complete conversion.

Table 2.5. Residual MEHQ levels in selected superabsorbent polymer samples from eight manufacturers, over several years

Manufacturer Designation	MEHQ Content (ppm)
A	151, 67
B	109
C	32, 84
D	94, 46
E	46
F	54, 32
G	33
H	30, 34, 16

These three factors all indicate that MEHQ behaves like a retarder in this system. In other words, the reaction described in Eq. 2.13 would be significant but would not prevent considerable "normal" polymerization from occurring. Referring to Eq. 2.14, this would be a situation in which the third term $k_z[Z][RM]$ dominates the second term $2k_t[RM]^2$ sufficiently to reduce the rate by lowering the radical concentration. This in turn would imply that $[RM]$, and hence the polymerization rate, would depend on the *first power of initiator concentration*. In addition, one would expect chain termination by a small molecule (Eq. 2.13) to result in half the average molecular weight seen with normal recombination of growing polymer chains.

However, it was found that the rates of polymerization at various levels of MEHQ and persulfate depend approximately on the half power of the initiator, as would be expected for an uninhibited reaction. Furthermore, molecular weights show either little change with increased inhibitor level or actually appear to increase. These deviations from the expected retardation behavior can be accommodated by a novel mechanism described in Eqs. 2.24 and 2.25 (this approach was originally proposed to us by D.J. Arriola of The Dow Chemical Co.). If the radical originating from the initiator fragment $R\cdot$ has a noticeably different reactivity with the inhibitor or the monomer from that of polymer-based radicals, the following reaction scheme should be used:



The reaction of $RM\cdot$ with Z (Eq. 2.13) does not occur to a significant extent, but the remainder of the polymerization follows the mechanism described in section 2.4.1.

The concentration of the initiator fragment $[R\cdot]$ is still at steady state, as in Eq. 2.26. Rearranging Eq. 2.26 results in an expression for the steady-state concentration of $[R\cdot]$, Eq. 2.27:

$$\frac{d[R\cdot]}{dt} = 2k_d[I] - k_z[R\cdot][Z] - k'[R\cdot][M] = 0 \quad (2.26)$$

$$[R\cdot] = \frac{2k_d[I]}{k_z[Z] + k'[M]} \quad (2.27)$$

Substituting this expression for the steady-state concentration of initiator radicals into Eq. 2.14 yields Eq. 2.28:

$$[RM\cdot] = \left(\frac{k_d[I]}{k_t} \right)^{1/2} \left(\frac{k_t[M]}{k_z[Z] + k_t[M]} \right)^{1/2} \quad (2.28)$$

By inverting and squaring Eq. 2.28, Eq. 2.29 is obtained:

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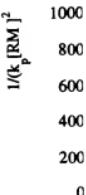


Figure 2.10. Dep
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$$\frac{1}{[RM]^2} = \frac{k_i}{k_d[I]} \left(1 + \frac{k_z[Z]}{k_i[M]} \right) \quad (2.29)$$

Largely independent of polymerization mechanism, a pseudo-first-order rate constant for a polymerization (i.e., the slope of the $\ln[M]$ vs. time curve) is equal to $k_p[RM]$, as apparent from Eq. 2.5. Different mechanisms primarily affect the value of $[RM]$. If one had pseudo-first-order rate constants at various inhibitor levels $[Z]$, but at a fixed series of initiator concentrations $[I]$, one could plot $1/(k_p[RM])^2$ vs. $[Z]$ for each $[I]$ and determine k_z/k_i . From experiments at fixed levels of inhibitor and varying, though irregular, levels of initiator, appropriate values of $k_p[RM]$ were interpolated for fixed initiator concentrations, and the plot described is shown in Figure 2.10. Values of k_z/k_i obtained from this plot are given in Table 2.6.

These values are remarkably constant. They are rather high compared with the values for the inhibition constant $z (= k_z/k_p)$ given by Odian.²⁶ We should note, however, that k_i in this case is probably significantly smaller than k_p . If k_i were equal to or greater than k_p , there would be no apparent effect of MEHQ on the kinetics, because nothing would "intercept" the initiator fragment but monomer. Since k_i must be smaller than k_p , k_z/k_i would be larger than the value expected for k_z/k_p from Odian's table.²⁶ This is the case, and thus there is internal consistency. In summary, the data are adequately explained if the MEHQ inhibitor is inferred to primarily intercept the initiator radical rather than the growing polymer radical.

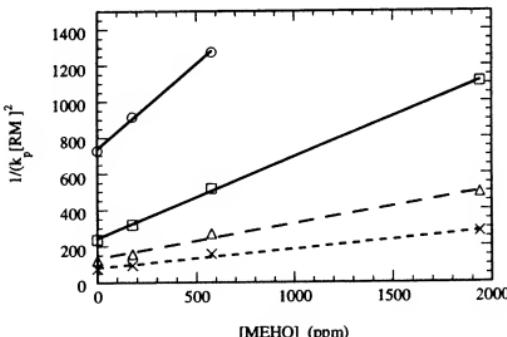


Figure 2.10. Dependence of inverse square of $k_p[RM]$ on the concentration of MEHQ for several values of $[I]$. $[I] = 0.0032$ (○), 0.0064 (□), 0.010 (Δ), 0.0144 (×).

Table 2.6. Calculated values of k_r/k_i for various initiator concentrations

Interpolated $[I]$ (mol/L)	k_r/k_i
0.0016	2.405
0.0036	3.506
0.0064	2.711
0.01	2.409
0.0144	2.523

2.5.4. Reactions Near Dryness

2.5.4.1. Continuation of Polymerization. Drying is an essential step in nearly every superabsorbent manufacturing process (see Chapter 3, section 3.2.5). Reactions normally studied in a polymerization reactor often continue during drying operations; events occurring in this regime may be particularly important in determining residual monomer levels in the final product. The impact on residual levels of the breakdown of co-polymerized acrylic acid dimer is discussed in section 2.2.2.2; but in the present section we consider the effect of the continuation of polymerization during drying. Both initiator and moisture levels are changing rapidly and independently of one another during drying, and this situation dramatically affects the polymerization rate of any remaining monomer. As an illustration of this interaction, a patent by Irie et al.⁵⁰ claims that the humidity of the drying air must be controlled so that polymer does not dry too quickly, thereby extending the polymerization reaction.

Studies of the rate of decrease in residual monomer concentration using nearly dry (down to 5% moisture) polymer samples held in closed vessels under nitrogen yield results that can be extrapolated from those obtained at reactor conditions. In other words, R_p is dependent on $[M]^{1/2}$ and $[I]^{1/2}$. In fact, at the increased solids content, the residual monomer can be reduced to undetectable levels under nitrogen. Similar studies of monomer reduction in closed systems in an air atmosphere show that oxygen inhibits this last bit of polymerization, as would be expected (S.S. Cutié et al., The Dow Chemical Co., unpublished results).

Very dry samples of sodium polyacrylate, for example, below 5% moisture, show reduced diffusion rates for moisture and oxygen. This can be interpreted as resulting from the transition of the polymer to a glassy state at reduced moisture. An inflection in the heat demand as measured by differential scanning calorimetry has been related to a glass transition temperature T_g (see Chapter 4, section 4.5.2.1). A plot of this inflection temperature versus the weight loss obtained from thermal gravimetric analysis for a series of sodium polyacrylate gel samples is shown in Figure 2.11 (A.J. Pasztor, Jr. et al., The Dow Chemical Co., unpublished results). The effect of the state of the reacting polymer gel, whether glassy or liquid, on other reactions is under study.

T_g (°C)

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